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A Vibrational Spectroscopy Study of  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COOD}$  and  $^{13}\text{CD}_3\text{COOH(D)}$

Adsorption on Pt(111): I. Surface Dimer Formation and Hydrogen Bonding

by

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To be published in: Surface Science

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A Vibrational Spectroscopy Study of  $\text{CH}_3\text{COOH}$ ,  
 $\text{CH}_3\text{COOD}$  and  $^{13}\text{CD}_3\text{COOH(D)}$  Adsorption on Pt(111):  
I. Surface Dimer Formation And Hydrogen Bonding

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## Abstract

Acetic acid ( $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COOD}$  and  $^{13}\text{CD}_3\text{COOH(D)}$ ) adsorption on Pt(111) at 168K has been studied as a function of surface coverage with HREELS. At low acetic acid dosages ( $\theta < 0.3$ ), dissociative adsorption occurs forming a surface acetate species with an  $\eta^2(\text{O},\text{O})\text{-CH}_3\text{COO}$  configuration in a  $\text{C}_s$  symmetry. Further dissociative adsorption as  $\text{CO}_{(\text{a})}$ ,  $\text{O}_{(\text{a})}$  and  $\text{CH}_x(\text{a})$  with  $x=1-2$  is observed for very low acetic acid dosages ( $\theta \sim 0.2$  or less). The formation of  $\text{HCOO}_{(\text{a})}$  or  $\text{CH}_3(\text{a})$  from acetic acid adsorption is ruled out based on the absence of their characteristic vibrational modes. Molecular adsorption occurs at moderate acetic acid dosages ( $\theta \sim 0.5$  or above) with a finger print peak at  $\sim 932 \text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  and  $^{13}\text{CD}_3\text{COOH}$  adsorbates. This mode corresponds to a well documented  $\gamma_{\text{OH}}$  mode of the acetic acid dimer. Hydrogen bonding between neighboring acetic acid molecules is responsible for the stabilization of the acetic acid hydroxyl group. The adsorbed acetic acid configuration is proposed to be a cyclic dimer with the dimer ring nearly parallel to the plane of metal surface. Quantitative correlations have been developed between the frequency of the  $\gamma_{\text{OH}}$  mode and the strength ( $\Delta H$ ) and bond length ( $R_{\text{O} \cdots \text{O}}$ ) of the hydrogen bond for a number of carboxylic acid dimers. Using these correlations from the literature our data can be used to estimate the hydrogen bond energy for acetic acid dimer on Pt(111) to be  $\sim 7.3 \text{ kcal/mole}$  with a corresponding estimate of the  $R_{\text{O} \cdots \text{O}}$  distance of  $\sim 2.68 \text{ \AA}$ .

## 1. Introduction

Acetic acid has been known to form hydrogen bonded cyclic dimers in the gas phase [1]. In the liquid phase, both cyclic and chain types of dimers are considered possible while in the solid crystal, infinite chains of hydrogen bonded structure of acetic acid has been reported[2-3]. As a continued effort to study the hydrogen bonding effects on surface chemistry, acetic acid has been chosen here following our studies of formamide surface chemistry. For the latter, hydrogen bonding and its influence on surface chemistry has been investigated on both Ni(111)[4] and Pt(111)[5].

The adsorption of acetic acid on transition metal surfaces has been the subject of several previous experimental investigations [6-11]. On Pt(111), a previous study has shown acetate species formation by oxygen pre-adsorption on the surface at low temperature [6]. The acetate species has also been reported on Cu(100) [7-8] and Al(111)[11] at low acetic acid exposures. A hydrogen bonded dimer form of acetic acid has been observed on Al(111) at high exposure ( $1.5 \times 10^{17}$  molecules/cm<sup>2</sup>), which is attributed to the physisorbed acetic acid molecules, from which we deduced that the adsorption is multilayer.

In our study, a systematic investigation is conducted to find the coverage dependence of hydrogen bonded species and the role it plays in surface chemistry. In order to have a clear vibrational mode assignments, isotopically labeled molecules of CH<sub>3</sub>COOD and <sup>13</sup>CD<sub>3</sub>COOH(D) are used in addition to CH<sub>3</sub>COOH for the HREELS and TDS experiments.

## 2. Experimental section

The experiments were performed in a two level UHV chamber with a base pressure of  $1 \times 10^{-10}$  torr. The upper level is equipped with low energy electron diffraction (LEED) optics, Auger electron spectrometer with cylindrical mirror analyzer, quadrupole

mass spectrometer, ion sputtering gun and sample doser. The lower level houses the high resolution electron energy loss spectrometer (HREELS).

An LK2000-14-R HREEL spectrometer was used for the vibrational analysis with a routine resolution of about  $30\text{ cm}^{-1}$  (FWHM of the elastic peak) for the clean Pt(111) surface. The spectral resolution did not degrade with acetic acid dosages within a monolayer coverage. A typical elastic beam counting rate at this resolution is about  $10^5$ - $10^6$  counts/sec. From LEED measurements, no surface ordering was found for acetic acid adsorption on Pt(111) which indicates the high performance quality of the HREEL spectrometer given the system studied is a *disordered overlayer*. The incident electron beam energy used is about 7 volt and the incident angle is 60 degree from the surface normal of the Pt(111) sample. Unless mentioned otherwise in the figure, the spectra were recorded in the specular direction.

The Pt(111) surface was oriented to within  $\pm 0.5^\circ$  of the desired (111) plane confirmed by both Laue X-ray diffraction and LEED. The surface cleanliness, following argon ion bombardments and oxygen treatments, was checked by both Auger electron spectroscopy (AES) and HREELS.

$\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COOD}$  and  $^{13}\text{CD}_3\text{COOH(D)}$  were obtained from Aldrich. The purity of  $\text{CH}_3\text{COOH}$  is 99.7%.  $\text{CH}_3\text{COOD}$  has 98 atom% D isotope purity and  $^{13}\text{CD}_3\text{COOH(D)}$  has 97.2 atom%  $^{13}\text{C}$ , 97.27 atom% D for methyl group and 43 atom% D for hydroxyl group. They are further purified in the gas dosing line by several freeze-pump-thaw cycles. A doser was used for acetic acid adsorption onto the front face of the cooled Pt(111) crystal. The doser consists of a 1/4" O.D. stainless steel tube whose orifice was located approximately 1 cm from the crystal surface. Reproducing the acetic acid coverages was accomplished by immediately rotating the crystal out of the acetic acid dosing beam after the pre-set dosing time. The effectiveness of dosing in this manner was confirmed by monitoring the reproducibility of the HREELS and the thermal desorption spectroscopy (TDS).

### 3. Results

#### 3.1 Adsorption of CH<sub>3</sub>COOH on Pt(111) at 168K

A set of Auger peak to peak ratios of C<sub>273</sub>/Pt<sub>237</sub> were measured as a function of CH<sub>3</sub>COOH dosage and the plot is shown in figure 1. This plot shows an abrupt change in slope at ~ 20 sec exposure time. The turning point for the slope change is assigned to monolayer exposure ( $\theta=1$ ) to establish a relative exposure scale. Our TDS results are consistent with this assignment which showed saturation exposure at this acetic acid dosage before the multilayer desorption peaks appear [12].

For the different CH<sub>3</sub>COOH dosages shown in figure 1, corresponding HREEL spectra have been taken. Figure 2 is a plot of some of these HREEL spectra measured at 168K as a function of increasing CH<sub>3</sub>COOH exposure. At initial small CH<sub>3</sub>COOH dosage ( $\theta \sim 0.03$ ) five vibrational modes are observed at 467, 661, 768, 1398 and 2057 cm<sup>-1</sup>, as shown in figure 2a. After increasing the CH<sub>3</sub>COOH dosage to  $\theta \sim 0.19$ , five more peaks occur at 302, 913, 1000, 2930 and 2988 cm<sup>-1</sup> (figure 2b). Substantial peak broadening as a function of increasing dosage is observed for the band at about 2940 cm<sup>-1</sup> (figure 2d-2h). At  $\theta \sim 0.30$  dosage (figure 2c), the previous peak at 2048 cm<sup>-1</sup> has disappeared accompanied by a drop of intensity of the 467 cm<sup>-1</sup> peak, and a new peak is observed at 874 cm<sup>-1</sup> (figure 2c) which later shifts to about 932 cm<sup>-1</sup> with increasing coverage. A weak peak at 1660 cm<sup>-1</sup> appears when CH<sub>3</sub>COOH dosage is above  $\theta \sim 0.5$  (figure 2d-2h). In figure 2f, a peak at 219 cm<sup>-1</sup> is observed. With larger exposure, this peak is not detected which could be caused by the loss of resolution of this band with the tail of the elastic peak since the instrumental resolution decreases when large exposures are used (before figure 2f, FWHM is about 30 cm<sup>-1</sup> for the elastic peak, after figure 2f, FWHM increases to ~ 40 cm<sup>-1</sup>). In all spectra shown in figure 2, the dominant peak is at ~1400 cm<sup>-1</sup>. The second dominant peak is at ~ 671 cm<sup>-1</sup> for CH<sub>3</sub>COOH dosages below  $\theta \sim 0.5$ .

When the acetic acid dosage exceeds  $\theta \sim 0.5$  the peak at  $932 \text{ cm}^{-1}$  becomes the second dominant peak.

A series of  $\text{CH}_3\text{COOH}$  spectra with relative exposure of 7.5 measured at 168K are plotted out as a function of off-specular scattering angle (figure 3). At 10 degree off-specular (figure 3d), a peak splitting is observed clearly at 605 and 698, 910 and 1003, 1318 and  $1400 \text{ cm}^{-1}$  as well as a peak intensity enhancement for the  $2927 \text{ cm}^{-1}$  band. With small initial exposure of  $\theta \sim 0.19$ , the off-specular spectrum is shown in figure 4, in which only one peak splitting is observed at 1340 and  $1400 \text{ cm}^{-1}$  (figure 4b).

### **3.2 $\text{CH}_3\text{COOD}$ adsorption on Pt(111) at 168K**

Three exposures of  $\text{CH}_3\text{COOD}$  have been recorded and the HREEL spectra are shown in figure 5. At low exposure ( $\theta \sim 0.63$ ), vibrational peaks are observed at 290, 464, 565, 680, 836, 942, 1029, 1156, 1388, 1660, 2038, 2910, 2979 and  $3037 \text{ cm}^{-1}$  (figure 5a), in which the dominant peak is at  $1388 \text{ cm}^{-1}$  and the second dominant peak is at  $680 \text{ cm}^{-1}$ . These two peaks change relative intensity at larger exposures as shown in figure 5b-5c where the  $687 \text{ cm}^{-1}$  peak becomes the strongest peak. Three peaks at 2910, 2979 and  $3037 \text{ cm}^{-1}$  become less well resolved and the peaks at 2038 and  $464 \text{ cm}^{-1}$  disappear with larger dosages (figure 5b-c).

### **3.3 $^{13}\text{CD}_3\text{COOH}$ adsorption on Pt(111) at 168K**

The isotopically labeled molecule  $^{13}\text{CD}_3\text{COOH(D)}$  has been studied with three relative exposures of 0.31, 1.25 and 3.75. The HREEL spectra are shown in figure 6a-c. At low dosages, peaks are observed at 225, 428, 661, 768, 903, 1049, 1176, 1388, 1602, 1902, 2058, 2203 and  $2261 \text{ cm}^{-1}$  (figure 6a). With larger dosages, the peaks at 428, 1902 and  $2058 \text{ cm}^{-1}$  disappear (figure 6b-c). The strongest peak is at  $388 \text{ cm}^{-1}$  with low dosage (figure 6a) and at  $661 \text{ cm}^{-1}$  with larger dosages (figure 6b-c).



## 4. Discussion

### 4.1 Acetic acid dosage vs. surface coverage at 168K

In figure 1, the Auger peak intensity ratio for  $C_{273}/Pt_{273}$  is plotted out as a function of increasing  $CH_3COOH$  dosage. A slope change has been observed at a relative exposure of 1.0. After this point, the  $C_{273}/Pt_{273}$  ratio grows very slowly with  $CH_3COOH$  dosage. This can be understood as follows. The  $CH_3COOH$  dosage below 1.0 is in the first monolayer coverage region so that the  $CH_3COOH$  molecules have high sticking probabilities due to the chemical interaction between the acetic acid adsorbate and the Pt(111) substrate. At about an exposure of 1.0, a monolayer of  $CH_3COOH$  is formed on the surface. After this point, the  $CH_3COOH$  molecules have lower sticking probabilities due to the weak van der Waals interaction between the acetic acid and the acetic acid covered substrate. This is indicated by a very slow increase of the  $C_{(273)}/Pt_{(237)}$  peak to peak ratio as a function of dosage. The high slope region corresponds to a chemisorption process while the small slope region corresponds to a physisorption process. The difference in adsorption nature is the cause for the change in sticking probabilities and thus, for the change of the slope in figure 1.

In our acetic acid adsorption experiments, the adsorption temperature of 168K is a little high for physisorbed multilayers to be stable which is observed from our TDS experiments [12]. The possible electron beam induced desorption has been considered during Auger data collection and efforts have been made to reduce this effect by using a relatively low beam voltage (1kV) and a low filament emission current (0.5 mA). With these electronic parameters the current measured at the crystal is  $\sim 4 \mu A$ . However, the nature of the bonding that changes the acetic acid sticking probability will not be altered given the presence of the electron beam induced desorption process. In our latter discussion, a coverage of  $\theta=1.0$  will refer the point at which this dramatic change of slope in figure 1 is obtained. If we assume a sticking probability of  $CH_3COOH$  molecules for chemisorption

to be one and 1 langmuir ( $1 \times 10^{-6}$  torr.sec) as the monolayer exposure, we estimate that our doser for acetic acid adsorption has a pressure enhancement factor of about 125. This  $\text{CH}_3\text{COOH}$  dosage and the surface coverage correlation is further supported by HREELS results. In figure 2f, the acetic acid dosage is 1.25 which is a little over monolayer exposure and the lattice mode of multilayer acetic acid at  $219 \text{ cm}^{-1}$  is observed. Below this dosage, we have not observed this mode which agrees that at 1.25 dosage multilayer starts to form. This mode for larger dosages is hard to detect due to the broadened elastic peak and its high background tail which interferes strongly with this low frequency mode at  $219 \text{ cm}^{-1}$ .

## 4.2 Acetate formation on Pt(111) at 168K

As we can see from figure 2, at low acetic acid dosage ( $\theta \sim 0.2$ ), the adsorption of  $\text{CH}_3\text{COOH}$  is dissociative. This is characterized by the lack of O-H related modes such as the stretching vibrational mode ( $\nu_{\text{OH}}$  is at  $3640 \text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  monomer[13]), O-H in plane bending mode ( $\delta_{\text{OH}}$  is at  $1176 \text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  monomer [13]) as well as O-H out of plane bending mode ( $\gamma_{\text{OH}}$  is  $650 \text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  monomer [14]). The absence of these O-H bond related vibrational modes in the HREEL spectra strongly suggests that the O-H bond of the acetic acid molecule is cleaved upon adsorption on Pt(111) at 168K, resulting in the acetate formation on Pt(111). The acetate species has also been identified for oxygen pre-exposed Pt(111) by Avery[6] in which it was intended to generate acetate species by enhancing the Bronsted basicity of the metal surface with pre-adsorption of oxygen. Our results indicate that even without oxygen preadsorption, the Pt surface has enough basicity to react with acetic acid forming surface acetate. The acetate species has also been reported by Chen et. al. on Al(111)[11], by Bowker et al. on Cu(110) [10] and by Sexton on Cu(111)[7-8].

The comparison of the vibrational frequencies of the acetate species is given in table 1 in which our result and the results from aqueous solution, Al(111), Cu(100) and oxygen preadsorbed Pt(111) are listed. The assignments for surface acetate vibrational

modes on Pt(111) at 168K are as follows: C-H stretching ( $\nu_{CH}$ ) at 2988~2930, symmetric COO stretching ( $\nu_{sCOO}$ ) at 1398  $cm^{-1}$ , CH umbrella bending mode ( $\delta_{CH_3}$ ) at 1340  $cm^{-1}$  (resolved from  $\nu_{sCOO}$  mode at 1398  $cm^{-1}$  with off-specular observation figure 4b), C-C stretching ( $\nu_{CC}$ ) at 1000  $cm^{-1}$ , in plane COO bending ( $\delta_{COO}$ ) mode at 671  $cm^{-1}$  and substrate platinum-oxygen of the acetate stretching vibration ( $\nu_{Pt-O}$ ) at 302  $cm^{-1}$ . The strong intensity for  $\nu_{sCOO}$ ,  $\delta_{COO}$  and  $\nu_{Pt-O}$  in the specular direction indicates that these modes are dipole active. The absence of  $\nu_{aCOO}$  in the specular spectra (figure 2a-c) indicates that this vibrational mode is dipole forbidden on the metal surface. This could be accounted for by an adsorption configuration of a bidentate acetate  $\eta^2(O,O)$ -CH<sub>3</sub>COO which is in a Cs symmetry. As explained by Sexton[7-8] and Chen et. al.[11], this configuration would give  $\nu_{sCOO}$ ,  $\delta_{COO}$  and  $\nu_{Pt-O}$  modes large dynamic dipole components perpendicular to the plane of the metal surface and hence strong on-specular peak intensities. The  $\nu_{aCOO}$  vibrational mode, however, will be weak since its dynamic dipole has little component perpendicular to the plane of the metal surface. These are consistent with the surface dipole selection rule i.e. only those vibrations with a non-zero dynamic dipole component perpendicular to the plane of metal surface will be observed with dipole scattering. The off-specular scattering is known to enhance the impact scattering mechanism. The  $\nu_{CH}$  and  $\delta_{CH_3}$  peaks are examples here. The spectra shown in figure 4b indicates that the  $\nu_{CH}$  mode at 2900-3000  $cm^{-1}$  and the  $\delta_{CH_3}$  mode at ~1340  $cm^{-1}$  are enhanced by off-specular observation. These two modes are thus considered to be impact scattering enhanced.

Apart from the acetate formation as discussed above, further dissociation of CH<sub>3</sub>COOH to CO<sub>(a)</sub> is observed as well. In figure 2a-b,  $\nu_{CO}$  and  $\nu_{Pt-CO}$  are observed at 2057  $cm^{-1}$  and 467  $cm^{-1}$ , respectively. These two peaks disappear for larger dosages (figure 2c-e). The small peak at ~413  $cm^{-1}$  in figures 2e-g is the out of plane bending mode of the COO group ( $\rho_{COO}$ ) in molecularly adsorbed acetic acid molecules. The formation of the adsorbed CO is clearly from the dissociation of CH<sub>3</sub>COOH rather than from the chamber background CO adsorption since no such modes are observed prior to

CH<sub>3</sub>COOH adsorption. Our temperature dependent HREELS and thermal desorption results also indicate that CO is a direct dissociation product from CH<sub>3</sub>COOH at elevated temperatures[12]. The presence of a CO<sub>(a)</sub> fragment from CH<sub>3</sub>COOH dissociation hints that further bond scission other than the O-H bond is possible at this adsorption temperature of 168K. Apparently, the C-C bond and C-O bond are broken to form CO<sub>(a)</sub>. We have ruled out the presence of HCOO<sub>(a)</sub> and CH<sub>3</sub>(a) species. For the HCOO<sub>(a)</sub> species, the literature indicates that the  $\nu_{\text{SCOO}}$  mode is in the range of 1330-1350 cm<sup>-1</sup> [15-22] while the CH<sub>3</sub>COO<sub>(a)</sub> species has  $\nu_{\text{SCOO}}$  at 1398-1470 cm<sup>-1</sup> [6-8, 11]. This is about 100 cm<sup>-1</sup> higher than the corresponding mode in HCOO<sub>(a)</sub>. The  $\delta_{\text{COO}}$  mode is at 760-785 cm<sup>-1</sup> for the HCOO<sub>(a)</sub> species while the CH<sub>3</sub>COO<sub>(a)</sub> species has  $\delta_{\text{COO}}$  at 650-675 cm<sup>-1</sup> which is about 100 cm<sup>-1</sup> lower than the corresponding mode in HCOO<sub>(a)</sub>. The lack of a  $\delta_{\text{SCH}_3}$  vibration, which has been reported to be a strong mode at ~1200 cm<sup>-1</sup> for CH<sub>3</sub>(a) [23-24], indicates that the surface CH<sub>3</sub>(a) species is possibly not stable in our experimental conditions. The surface CH<sub>2</sub>(a) group has been reported on Ru(001)[25] with strong peaks at 2940 ( $\nu_{\text{SCH}_2}$ ) and 1450 cm<sup>-1</sup> ( $\delta_{\text{SCH}_2}$ ). In figure 2b, modes at 2930, 2988 and 1398 cm<sup>-1</sup> may have contributions from surface CH<sub>2</sub>(a) species. CH<sub>(a)</sub> species may also present since this species gives  $\nu_{\text{CH}}$  modes at 3050 cm<sup>-1</sup> and  $\delta_{\text{CH}}$  mode at 770 cm<sup>-1</sup> [26-27]. We have observed weak peaks at 2988 cm<sup>-1</sup> and 768 cm<sup>-1</sup> (figure 2a,b) which could be from CH<sub>(a)</sub>. The peak at 768 cm<sup>-1</sup> in figure 2a is also present with <sup>13</sup>CD<sub>3</sub>COOH(D) adsorption at low dosage (figure 6a), which indicates that apart from the possible CH<sub>(a)</sub> other species may have contributions to this peak. The most probable one is O<sub>(a)</sub> since this species is also a counter part of CO<sub>(a)</sub> from CH<sub>3</sub>COOH dissociative adsorption, and on Pt(111) this mode has been observed at 750-800 cm<sup>-1</sup> with Ca impurities[28]. Thus, we observe CH<sub>3</sub>COOH dissociatively adsorbed on Pt(111) at low dosages forming surface acetate (CH<sub>3</sub>COO<sub>(a)</sub>) and surface H<sub>(a)</sub>. Acetate species could further decompose to CO<sub>(a)</sub>, O<sub>(a)</sub> and CH<sub>x</sub> species with x=1-2 at very low acetic acid dosage.

### 4.3 Molecular adsorption of acetic acid on Pt(111) at 168K

Non-dissociative molecular adsorption of acetic acid occurs after the Pt(111) surface is passivated by the species from acetic acid dissociation. When the acetic acid dosages exceed  $\theta \sim 0.5$  new features of the vibrational spectra grow in at  $932\text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}/\text{Pt}(111)$  (figure 2d-h) and at  $913\text{ cm}^{-1}$  for  $^{13}\text{CD}_3\text{COOH(D)}/\text{Pt}(111)$  (figure 6b-c). With more exposure, the peak intensity increases and exceeds the  $\delta_{\text{COO}}$  mode ( $\sim 678\text{ cm}^{-1}$ ) as the second dominant peak (figure 2d-h). The width of this peak also increases as a function of increasing dosage. All these phenomena are not observed for deuterium substituted OH group molecule  $\text{CH}_3\text{COOD}$  in figure 5a-c. Thus, we conclude that peaks at  $932\text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  adsorbate and  $913\text{ cm}^{-1}$  for  $^{13}\text{CD}_3\text{COOH(D)}$  adsorbates are related to the hydroxyl group (OH). After literature studies it turns out that this peak originates from the out of plane bending mode for the OH group ( $\gamma_{\text{OH}}$ ) from acetic acid cyclic dimers which we will discuss in detail later. We would like to point out here that due to the strong hydrogen bonding between neighboring acetic acid molecules and possibly between acetic acid and acetate species, the  $\nu_{\text{OH}}$  mode is no longer characteristic for molecular adsorption identification. The "free" OH stretching frequency ( $\nu_{\text{OH}}$ ) for the acetic acid molecule in the gaseous state at 430K is observed at  $3583\text{ cm}^{-1}$  [29]. It decreases to a broad peak near  $2900\text{ cm}^{-1}$  in the acetic acid crystal near 90K[29] and is hard to differentiate from the C-H stretching peak which also falls in this region. The  $\nu_{\text{OH}}$  can vary from 2900 to  $3100\text{ cm}^{-1}$  for liquid  $\text{CH}_3\text{COOH}$  with temperature and solvents due to their influence on the strength of hydrogen bonding[30]. It is thus not surprising that different  $\nu_{\text{OH}}$  frequencies have been reported in the literature. However, the  $\gamma_{\text{OH}}$  mode is found to be characteristic [31] and thus is used here as a indicator of the presence of molecular adsorption. The  $\gamma_{\text{OH}}$  mode is observed with a dosage of  $\theta \sim 0.5$  (figure 2d). With the presence of the  $\gamma_{\text{OH}}$  mode at  $\sim 932\text{ cm}^{-1}$ , the peak in the  $2900\text{-}3020\text{ cm}^{-1}$  region becomes broadened (figure 2d-g) which we assume is due to contributions from  $\nu_{\text{H-O-H}}$  in this region. On the Al(111)

surface  $\nu_{\text{H-O-H}}$  has been observed at  $2740\text{ cm}^{-1}$  for multilayer  $\text{CH}_3\text{COOH}$  adsorption[11]. The asymmetric shape in figure 2g at  $2917\text{ cm}^{-1}$  with a shoulder at  $2958\text{ cm}^{-1}$  and the off-specular spectra shown in figure 3 leads us to tentatively assign those peaks above  $2950\text{ cm}^{-1}$ , at large dosages, as the  $\nu_{\text{H-O-H}}$  mode since  $\nu_{\text{C-H}}$  is believed to be enhanced in off-specular scattering which is observed below  $2950\text{ cm}^{-1}$  in figure 3. However, as we have mentioned above, the assignment for this mode is not conclusive.

Comparing the coverage dependent HREEL spectra of  $\text{CH}_3\text{COOH}$ (figure 2),  $\text{CH}_3\text{COOD}$  (figure 5) and  $^{13}\text{CD}_3\text{COOH(D)}$  (figure 6), we have assigned the  $1034\text{ cm}^{-1}$  band in figure 2, the  $1039\text{ cm}^{-1}$  band in figure 5 and the  $1039\text{ cm}^{-1}$  band in figure 6 to a C-C stretching vibration. The alternative assignment of this band to out-of-plane  $\text{CH}_3$  bending ( $\rho_{\text{CH}_3}$ ) [32] or OH in plane bending ( $\delta_{\text{OH}}$ ) [13] dose not seem appropriate here since this peak does not show a significant shift upon deuteration of either the methyl or the hydroxyl group.

The band at  $\sim 1660\text{ cm}^{-1}$  (figure 2d) is very weak in intensity. This mode is not detected for small dosages (figure 2a-c). The acetic acid isotope adsorptions have not resulted in significant shifts of this peak. For  $\text{CH}_3\text{COOD}$  adsorption, this band is at  $1631\text{--}1660\text{ cm}^{-1}$  and for  $^{13}\text{CD}_3\text{COOH}$  adsorption, this band is at  $1600\text{--}1640\text{ cm}^{-1}$ . Thus, we can rule out a hydrogen related vibration for this band. A possible assignment for this band is from the carbonyl stretching mode ( $\nu_{\text{C=O}}$ ) of the acetic acid dimers since with low dosages where the surface is dominated by acetate species, this mode is not detected (figure 2a-c). When the acetic acid dosages exceed the dimer formation range ( $\theta \sim 0.5$ ) this mode is observed in on-specular scattering (figure 2d-h, figure 5a-c and figure 6b-c). A carbonyl stretching mode at  $\sim 1660\text{ cm}^{-1}$  has also been reported by Bellamy et. al.[30] which supports our assignment.

Strong bands at  $\sim 1400\text{ cm}^{-1}$  for  $\text{CH}_3\text{COOH}$  (figure 2d-h), at  $\sim 1388\text{ cm}^{-1}$  for  $\text{CH}_3\text{COOD}$  (figure 5a-c) and at  $\sim 1383\text{ cm}^{-1}$  for  $^{13}\text{CD}_3\text{COOH(D)}$  have two sources of contribution. At small dosages where acetate species dominate the surface, this band corresponds to  $\nu_{\text{S-COO}}$  mode of the acetate species. At large dosages where both

acetate and acetic acid dimers are present,  $\delta_{\text{CH}_3}$  mode of the acetic acid can also contribute to this peak. We consider that  $\nu_{\text{SCOO}}$  mode of the acetate species is the major contributor for this peak due to the lack of isotope shift of this band when methyl group is substituted by D.

Table 2 has summarized the mode assignments for molecularly adsorbed acetic acid. Our peak assignments and those of gas phase acetic acid [13] and acetic acid adsorbed on Al(111) [11] are listed as well.

#### 4.4 Hydrogen bonding and acetic acid dimerization

In the introduction, we have mentioned our motivation for the study of acetic acid adsorption on Pt(111). Our previous studies of hydrogen bonding effects were conducted on formamide ( $\text{HCONH}_2$ ) on Ni(111)[4] and on Pt(111)[5]. In the  $\text{HCONH}_2/\text{Ni}(111)$  system, hydrogen bonding has been considered to influence the adsorption geometry of the formamide molecules which leads to two parallel reaction channels. For the  $\text{HCONH}_2/\text{Ni}(111)$  and  $\text{HCONH}_2/\text{Pt}(111)$  systems, red shifts and broadening of the  $\nu_{\text{NH}}$  peak are observed and a dimer form of  $\text{HCONH}_2$  was proposed. In this work for the acetic acid /Pt(111) system, we also observed strong hydrogen bonding between adsorbed acetic acid species which is indicated by the presence of a substantially blue shifted  $\gamma_{\text{OH}}$  mode of the dimer form of acetic acid.

Hydrogen bonding in the liquid and solid phase has been extensively studied[33]. However, not much attention has been given to hydrogen bonding effects in surface adsorption and surface reactions. Apart from the  $\text{HCONH}_2/\text{Ni}(111)$  and  $\text{CH}_3\text{COOH}/\text{Pt}(111)$  systems in which hydrogen bonding effects are focused, Key et. al.[34] have studied  $\text{H}_2\text{O}$ , HF, and  $\text{NH}_3$  adsorption. They have observed that hydrogen bonding could shift sub-monolayer TDS peaks to higher temperatures and could change the order of the desorption kinetics. Since surface chemistry mostly concerns the first monolayer of adsorbed species, the hydrogen bonding in the first monolayer appears to be more important than the hydrogen bonding formed in multilayers which is

physisorption in nature and in many ways similar to the solid phase of the molecule. In our studies, the onset of  $\gamma_{OH}$  mode at  $932\text{ cm}^{-1}$  appears at  $\theta \sim 0.5$ . This mode is significantly blue shifted ( $\Delta\nu \sim 282\text{ cm}^{-1}$ ) from the corresponding peak of the monomer ( $\sim 650\text{ cm}^{-1}$ ) and thus is assigned as the dimer  $\gamma_{OH}$  mode. This mode from the dimer form of different carboxylic acid molecules has been extensively studied as indicated in the literature (3, 4, 29, 31, 35, 36). The relative intensity of the  $\gamma_{OH}$  mode (relative intensity to the elastic peak of incident electron beam) as a function of dosage is plotted in figure 7. From this plot, it is deduced  $\theta \sim 0.3$  is the onset of surface hydrogen bond formation. On deuteration of the hydroxyl group, the  $\gamma_{OD}$  mode falls into the  $\delta_{COO}$  peak region as shown in figures 5b-c in which the peak at  $687\text{ cm}^{-1}$  becomes the strongest peak with large  $\text{CH}_3\text{COOD}$  dosages. We consider that the peak at  $687\text{ cm}^{-1}$  has contributions from two sources. One is the  $\delta_{COO}$  mode and the other is the  $\gamma_{OD}$  mode. Without the contribution of the latter,  $\nu_{sCOO}$  at  $\sim 1398\text{ cm}^{-1}$  would always be the dominant peak with all dosages as is seen for  $\text{CH}_3\text{COOH}$  molecules (figures 2a-h). The strongest peak of  $^{13}\text{CD}_3\text{COOH(D)}$  adsorption in figure 6b-c is also at  $\sim 661\text{ cm}^{-1}$  which is expected since 57 atom% D composed for the hydroxyl group. Also, the deuteration on methyl group has removed the  $\delta_{CH_3}$  contribution to the  $1383\text{ cm}^{-1}$  band and thus the  $1383$  to  $661\text{ cm}^{-1}$  peak intensity ratio is reduced.

The characteristic  $\gamma_{OH}$  mode for acetic acid dimers has been correlated to the strength of the hydrogen bonding energy[14] and the  $\text{OH}\cdots\text{O}$  bond length[31]. From our results of  $\gamma_{OH}$  at  $\sim 932\text{ cm}^{-1}$  using this correlation we can estimate that the hydrogen bond strength  $\Delta H$  to be  $\sim 7.3\text{ kcal/mole}$  (referenced to monomer  $\gamma_{OH}$  at  $650\text{ cm}^{-1}$ [14]) and the  $\text{R}_\text{O}\cdots\text{O}$  distance to be  $\sim 2.68\text{\AA}$ .

The presence of adsorbed monomer of acetic acid is not likely since for monomer the  $\nu_{OH}$  mode should be at  $\sim 3583\text{ cm}^{-1}$  and  $\gamma_{OH}$  mode should be at  $\sim 650\text{ cm}^{-1}$ [14]. Neither of these modes is observed in our experiment.



#### 4.5 Off-specular scattering and the dimer form of acetic acid

The surface selection rule indicates that a large perpendicular dynamic dipole component will give a strong peak in specular scattering (dipole scattering). The peak intensity would decrease dramatically as a function of off-specular scattering angle. The  $\nu_{\text{CO}}$  peak has been accepted as exhibiting a dipole scattering mechanism [37]. Figure 8 plots out the variation of  $\nu_{\text{SCOO}}$ ,  $\delta_{\text{COO}}$  and  $\nu_{\text{CH}}$  peak intensities relative to the  $\nu_{\text{CO}}$  peak intensity as a function of off-specular angle when all of these modes are present for  $\text{CH}_3\text{COOH}$  adsorption. It can be seen that as the off-specular angle increases, the  $\nu_{\text{SCOO}}$  and  $\delta_{\text{COO}}$  peak intensities drop even faster than that of the  $\nu_{\text{CO}}$  peak indicating that  $\delta_{\text{COO}}$  and  $\nu_{\text{SCOO}}$  peaks are dominated by dipole scattering. The  $\nu_{\text{CH}}$  peak shows intensity enhancement relative to the  $\nu_{\text{CO}}$  peak with increasing off-specular angle suggesting that the  $\nu_{\text{CH}}$  peak is dominated by the impact scattering mechanism. This is consistent with the general conclusion that the  $\nu_{\text{CH}}$  mode has a property of off-specular enhancement [37]. Figure 9 is a plot of both  $\gamma_{\text{OH}}$  and  $\nu_{\text{CH}}$  peak intensities relative to the dipole dominant  $\nu_{\text{SCOO}}$  peak intensity as a function of off-specular angle. The decrease of  $\gamma_{\text{OH}}$  peak vs.  $\nu_{\text{SCOO}}$  peak intensity ratio with off-specular scattering angle indicates that OH out of plane bending mode is also dominated by dipole scattering. This implies that the OH bending motion should have a strong perpendicular dynamic dipole component. In figure 10, we propose a cyclic dimer form of acetic acid adsorption configuration. This dimer form has the dimer ring nearly parallel to the metal surface and would thus give a strong perpendicular dynamic dipole component for OH out of plane bending motion. The C-C bond is tilted from the surface normal which agrees with the weak on-specular  $\nu_{\text{CC}}$  peak ( $\sim 1035\text{ cm}^{-1}$ ) and possibly the weak on-specular CH bond related modes. This configuration can also account for the presence of a weak carbonyl stretching mode ( $\nu_{\text{C=O}}$ ) at  $\sim 1660\text{ cm}^{-1}$  since the  $\nu_{\text{C=O}}$  motion will give a non-zero but small perpendicular dynamic dipole component. The shift of the  $\nu_{\text{C=O}}$  mode from  $1717\text{ cm}^{-1}$  to  $1660\text{ cm}^{-1}$  in the temperature dependent liquid  $\text{CH}_3\text{COOH}$  IR spectra has been

interpreted as a systematic change from the open chain form to the cyclic dimer form [30] which is consistent with our proposed cyclic dimer form of acetic acid adsorption. While a chain form of hydrogen bonded acetic acid is possible, the HREEL spectra of our experiment favor the cyclic dimer by comparison with the results of the known cyclic dimer IR spectra [30,31]. The onset of the dimer formation below monolayer coverage suggests that hydrogen bonding between the acetic acid molecule and acetate species is also possible, and the configuration of which would be similar to the cyclic dimer configuration in figure 10 with one of the H atom removed and all the rest of the configurations retained.

## 5 Summary

(1).  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COOD}$  and  $^{13}\text{CD}_3\text{COOH}$  adsorption on Pt(111) at 168K has been studied. The vibrational mode assignments are helped by isotope substitutions on both the methyl and the hydroxyl group of the acetic acid molecules leading to the mode assignments listed in table 1 and table 2.

(2). Acetic acid adsorption on Pt(111) at 168K exhibits both dissociative and non-dissociative adsorption. At very low dosage ( $\theta \sim 0.04$ ),  $\text{CH}_3\text{COOH}$  dissociates into surface acetate species in an  $\eta^2(\text{O},\text{O})\text{-CH}_3\text{COO}$  configuration. The acetate ion can further decompose into  $\text{CO}_{(\text{a})}$ ,  $\text{O}_{(\text{a})}$  and  $\text{CH}_{\text{x}(\text{a})}$  species with  $\text{x}=1\text{-}2$ .

(3) The acetate species ( $\text{CH}_3\text{COO}_{(\text{a})}$ ) is distinguishable from the formate species ( $\text{HCOO}_{(\text{a})}$ ) with their vibrational spectra. The former species has  $\nu_{\text{SCOO}}$  mode at  $1398\text{-}1470\text{ cm}^{-1}$  and  $\delta_{\text{COO}}$  at  $650\text{-}675\text{ cm}^{-1}$  while the latter species has  $\nu_{\text{SCOO}}$  mode at  $\sim 100\text{ cm}^{-1}$  lower and the  $\delta_{\text{COO}}$  mode at  $\sim 100\text{ cm}^{-1}$  higher than the corresponding mode for the former species.

(4). The onset of non-dissociative molecular adsorption of acetic acid at 168K is estimated to occur substantially at  $\theta \sim 0.4$  which is below the monolayer coverage. It is characterized by the OH out of plane bending mode of acetic acid dimer at  $\sim 932\text{ cm}^{-1}$ .

(5). The hydrogen bonded dimer configuration is proposed which fits the HREEL spectra characteristics. The hydrogen bonding strength of the dimer  $\Delta H$  is estimated to be  $\sim 7.3$  kcal/mole and the  $R_{(O \cdots O)}$  distance for hydrogen bonded dimer acetic acid is estimated to be  $\sim 2.68$  Å.

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## Figure Caption

Figure 1. Acetic acid Auger uptake curve, the acetic acid adsorption temperature is 168K, the chamber background pressure is  $5 \times 10^{-10}$  torr when the dosing beam is on.

Figure 2. Coverage dependent HREEL spectra of  $\text{CH}_3\text{COOH}$  on Pt(111)

with acetic acid adsorption at 168K and dosages of (a)  $\theta \sim 0.03$  (b)  $\theta \sim 0.19$

(c)  $\theta \sim 0.30$  (d)  $\theta \sim 0.50$  (e)  $\theta \sim 0.63$  (f)  $\theta \sim 1.25$  (g)  $\theta \sim 2.5$  (h)  $\theta \sim 7.5$

Figure 3. Off-specular spectra of  $\text{CH}_3\text{COOH}$  adsorption on Pt(111) at 168K with a dosage of  $\theta \sim 7.5$

Off-specular angles are: (a) 0 degree (b) 3 degree (c) 5 degree (d) 10 degree

Figure 4. Off-specular spectra of  $\text{CH}_3\text{COOH}$  adsorption on Pt(111) at 168K with a dosage of  $\theta \sim 0.19$  (a) on-specular (b) 5 degree off-specular

Figure 5. Coverage dependent HREEL spectra of  $\text{CH}_3\text{COOD}$  on Pt(111) with acetic acid dosages of (a)  $\theta \sim 0.63$  (b)  $\theta \sim 1.25$  (c)  $\theta \sim 3.75$

Figure 6. Coverage dependent HREEL spectra of  $^{13}\text{CD}_3\text{COOH(D)}$  adsorption on Pt(111) at 168K with acetic acid dosages of (a)  $\theta \sim 0.3$  (b)  $\theta \sim 1.25$  (c)  $\theta \sim 3.75$

Figure 7. The relative intensity of the  $\gamma_{\text{OH}}$  mode as a function of the acetic acid dosage

Figure 8. The relative intensities of the  $\nu_{\text{SCOO}}$ ,  $\delta_{\text{SCOO}}$  and  $\nu_{\text{CH}}$  modes as a function of the off-specular angle

Figure 9. The relative intensity ratios of  $\gamma_{\text{OH}}/\nu_{\text{SCOO}}$  and  $\nu_{\text{CH}}/\nu_{\text{SCOO}}$  as a function of the off-specular angle

Figure 10. Proposed cyclic acetic acid dimer adsorption configuration

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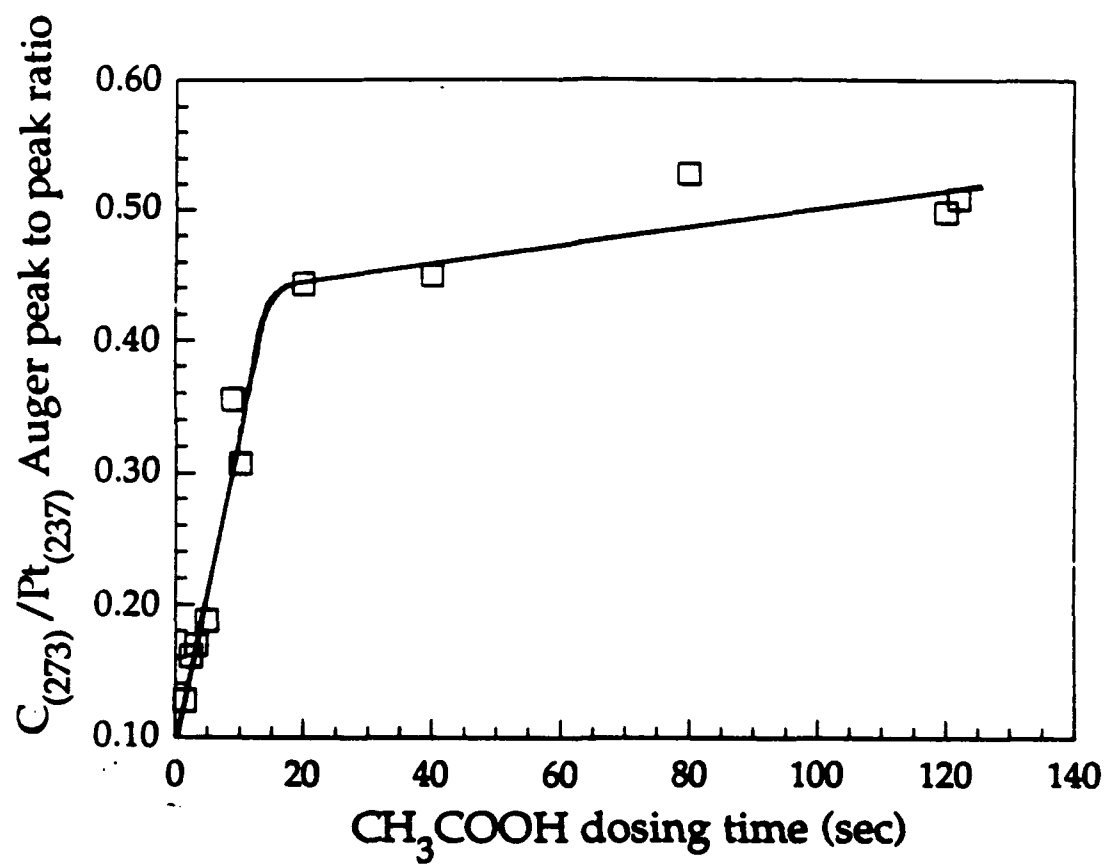
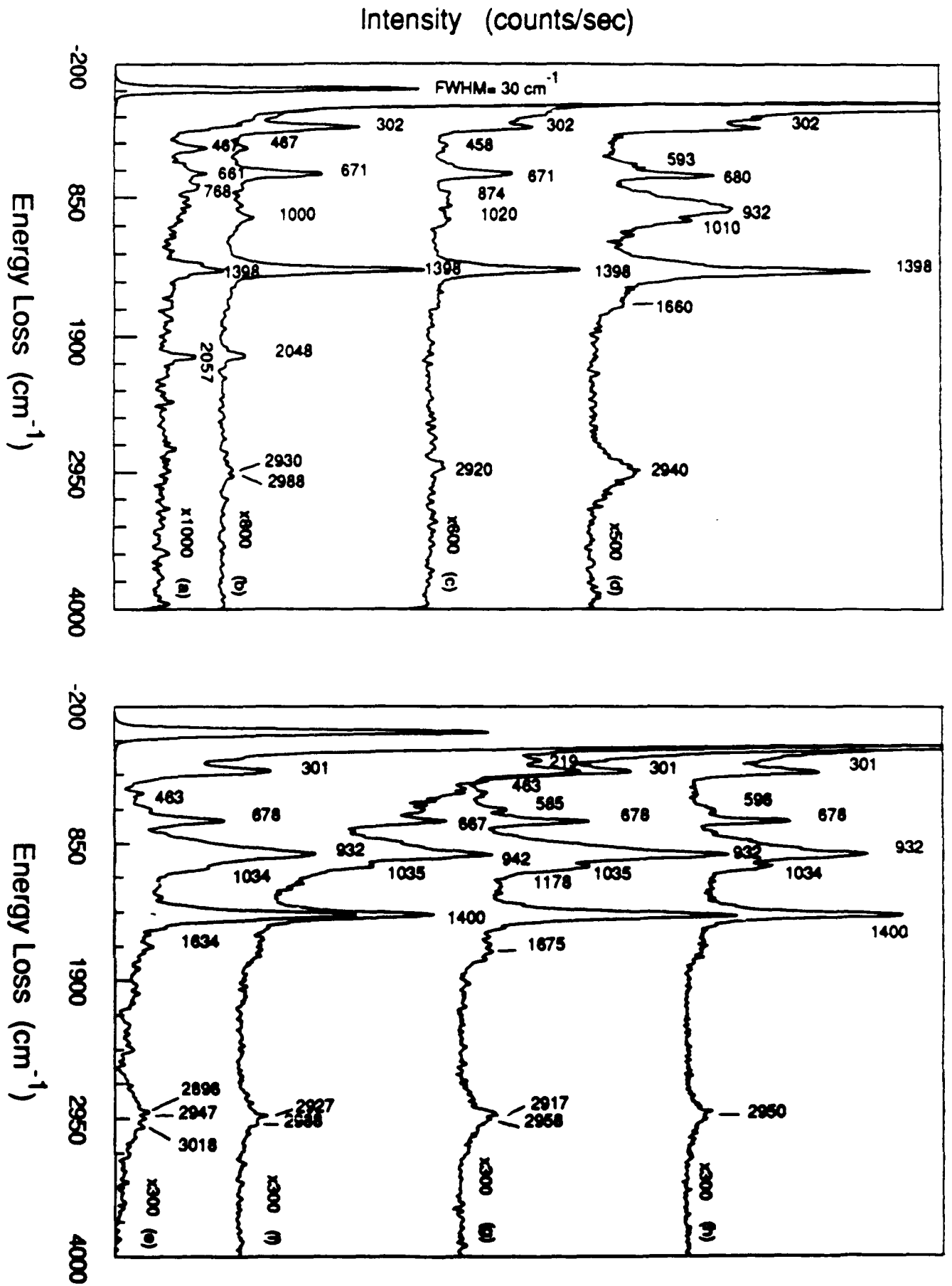


fig. 1

fig a.





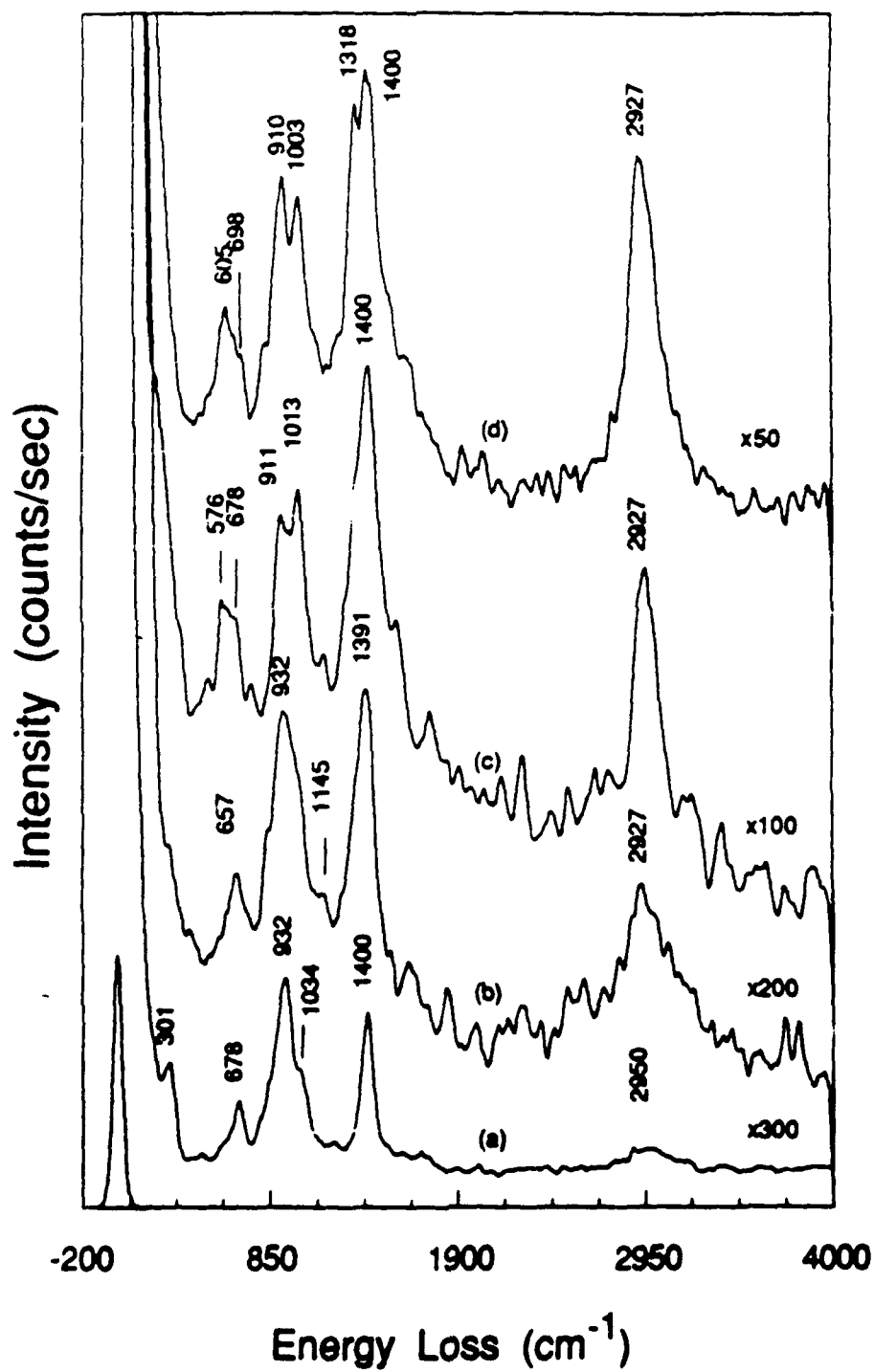


fig 3.

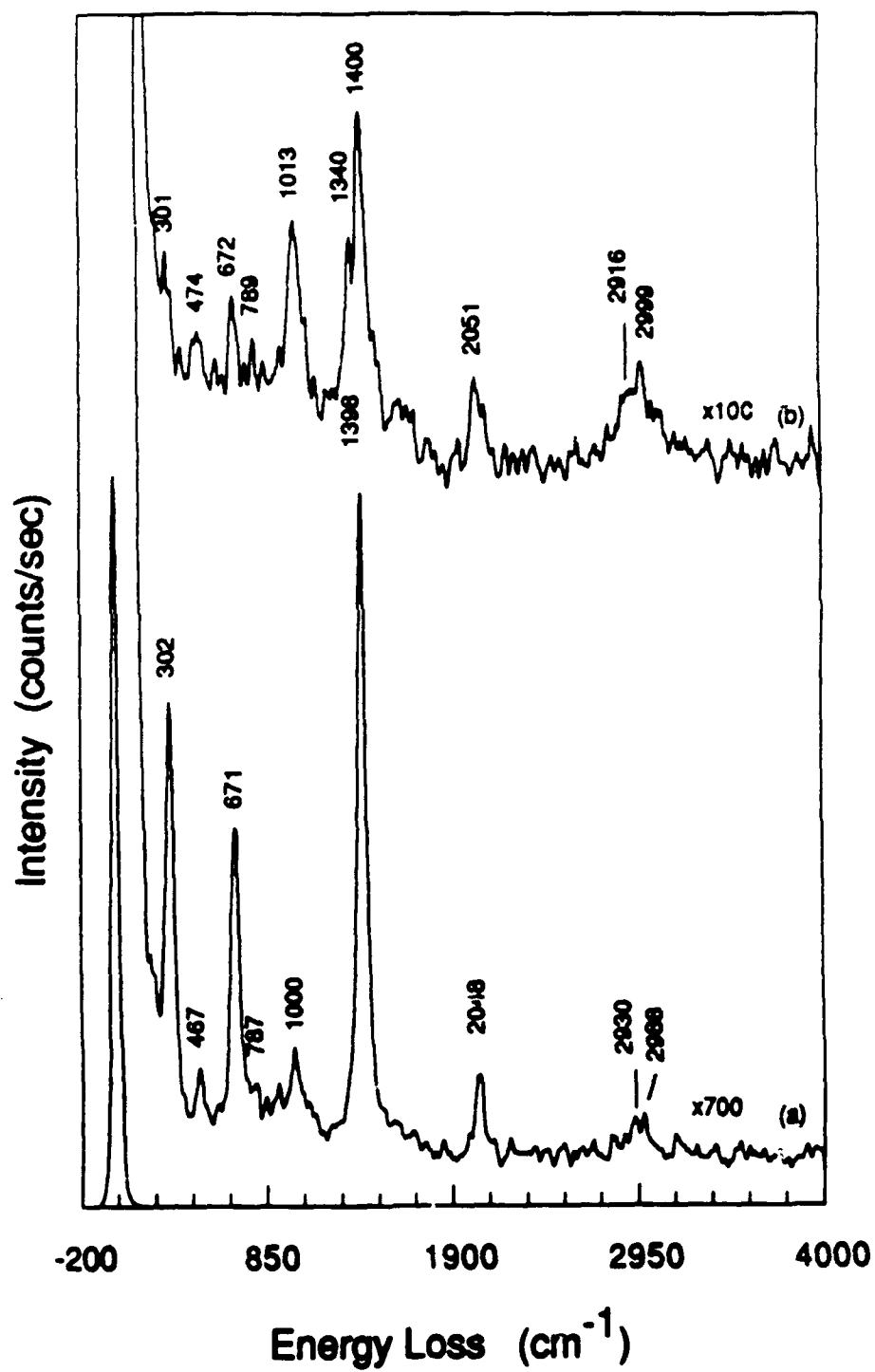


fig. 4

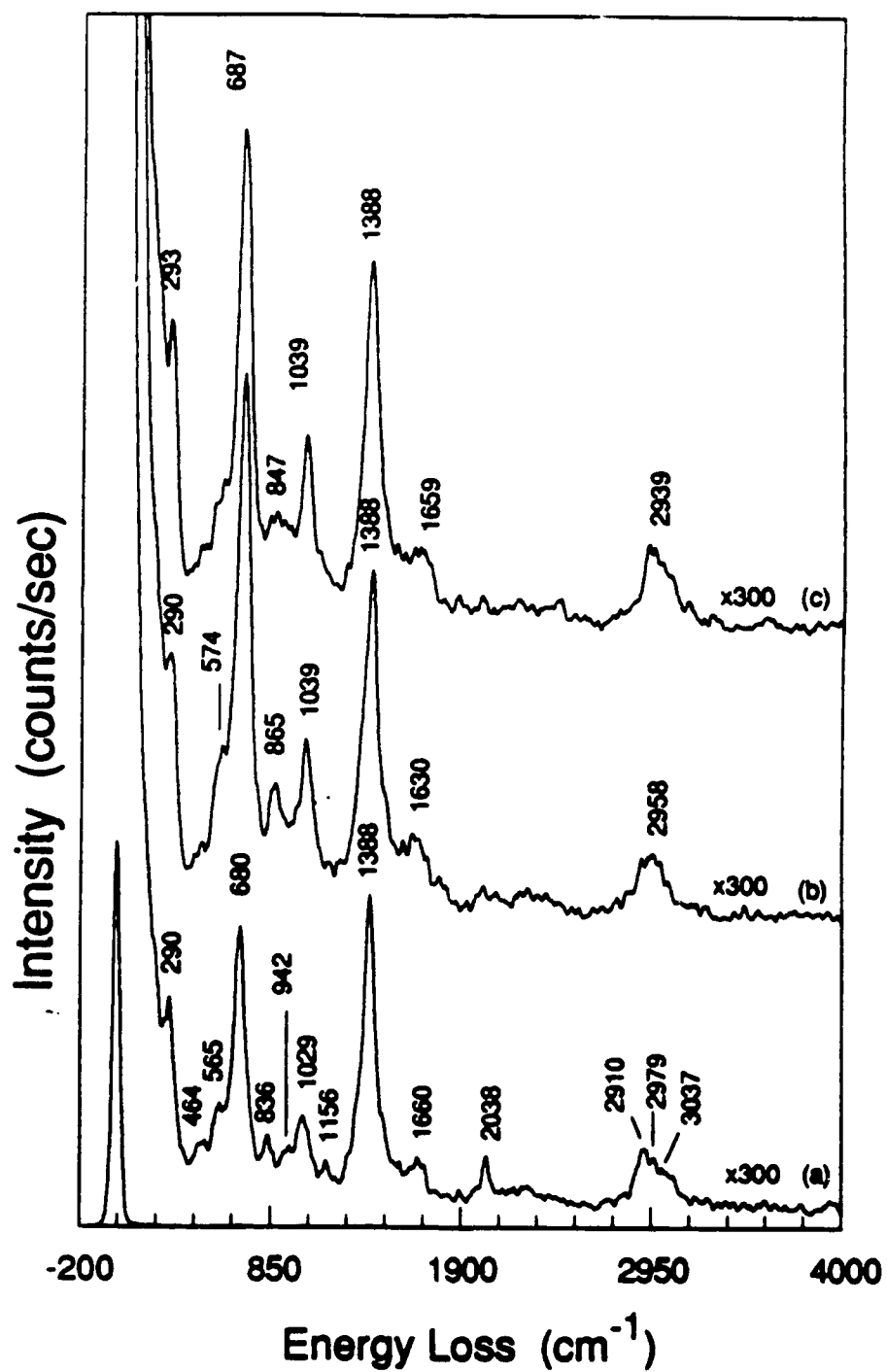


fig. 5

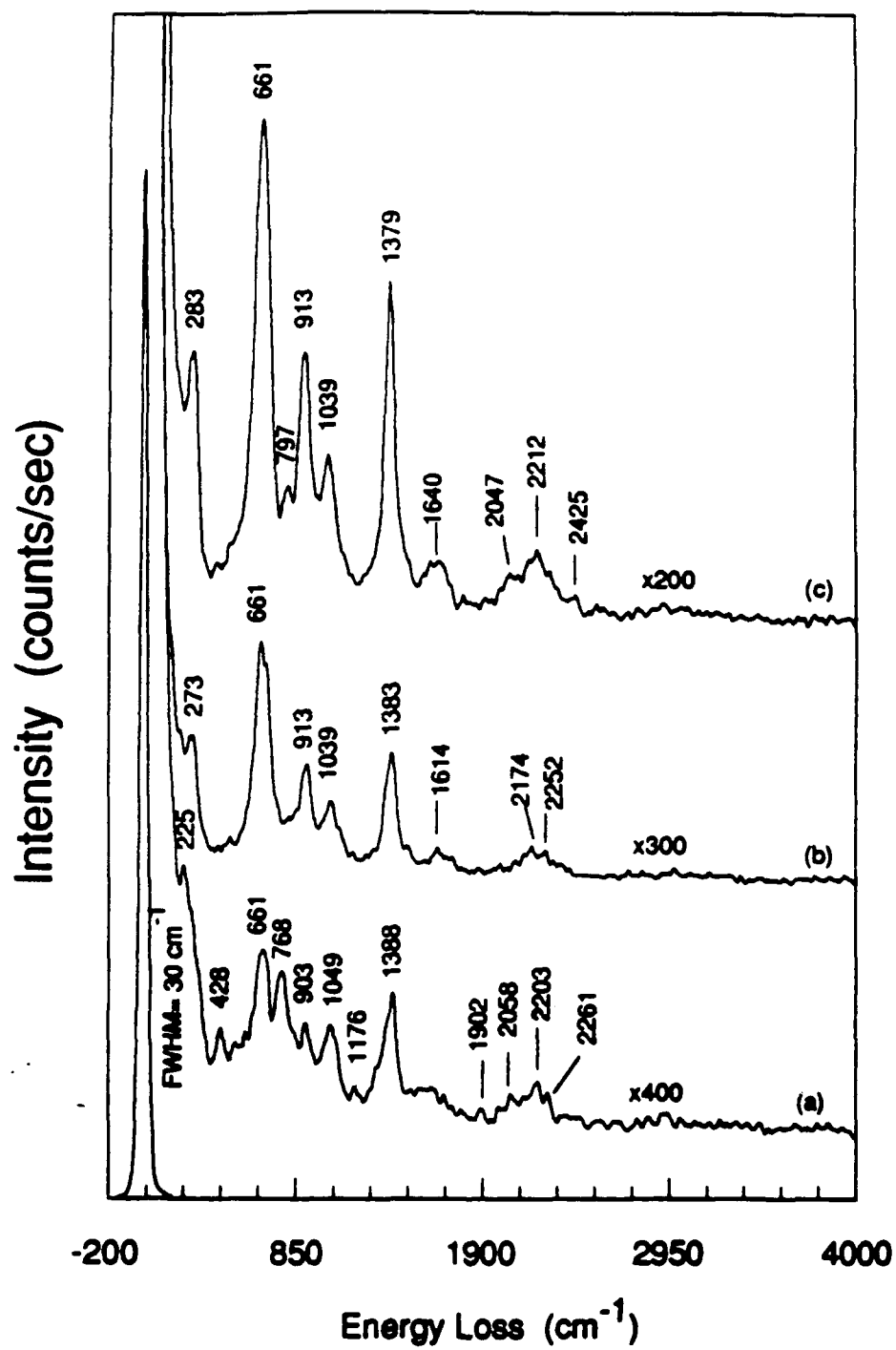


fig 6.

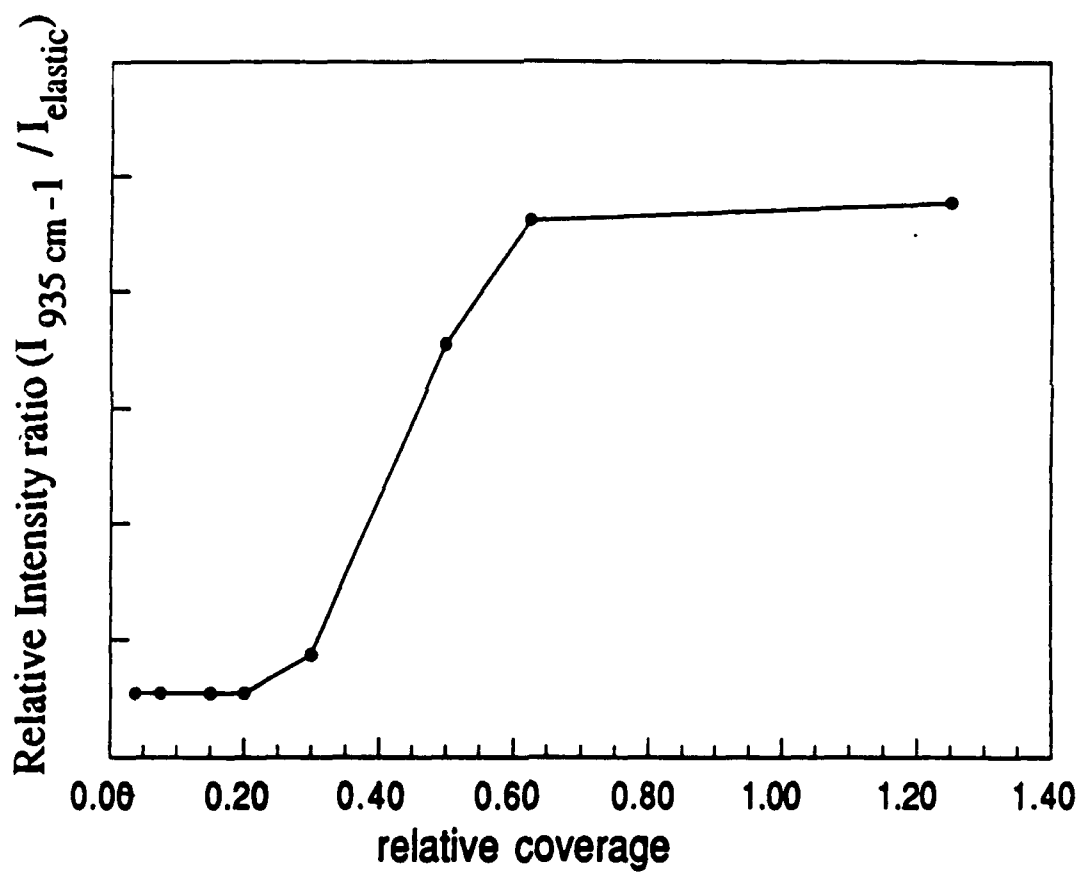


fig. 7

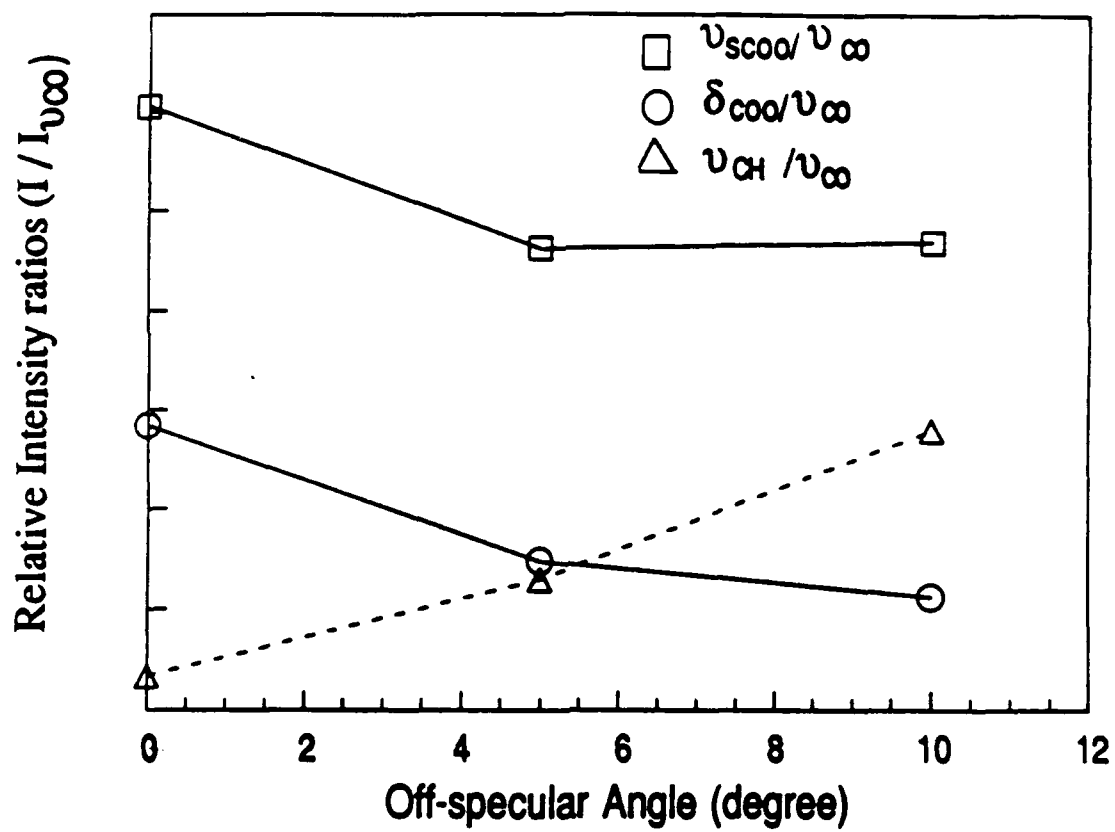


fig. 8

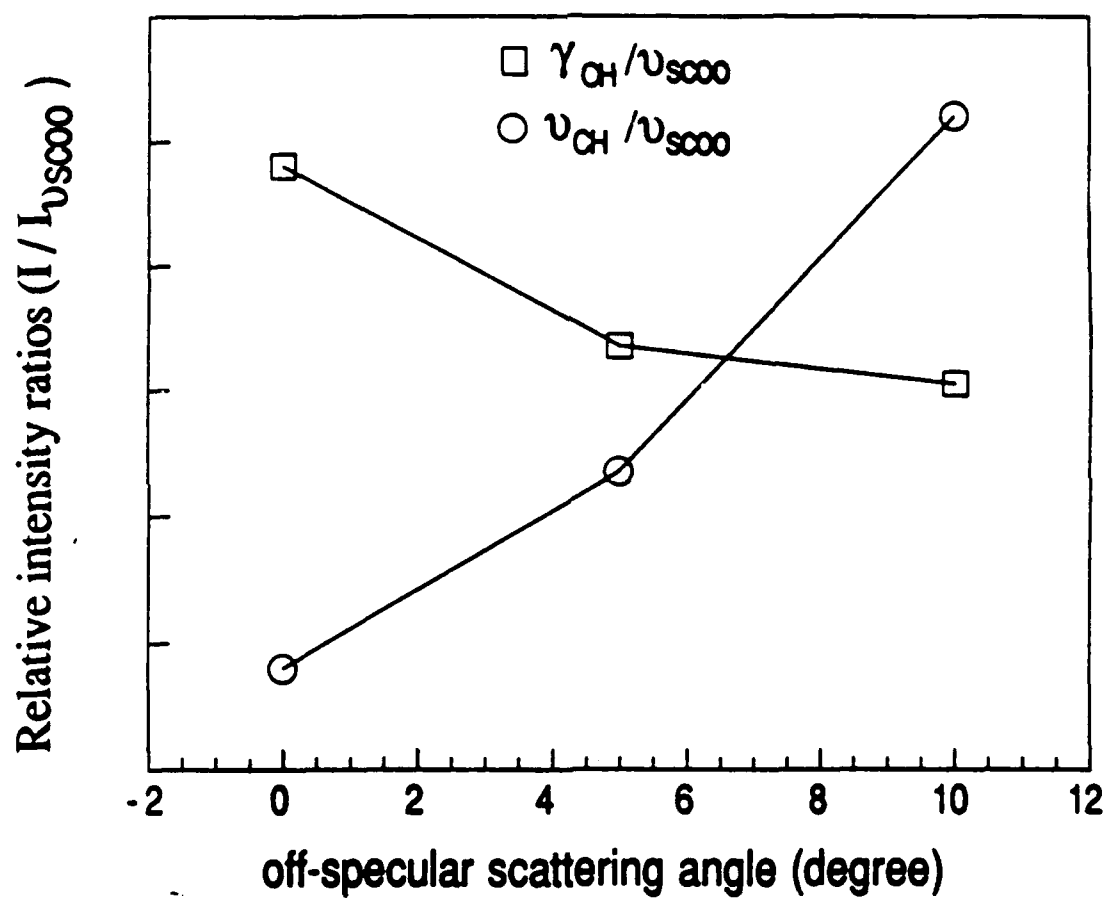


fig. 9

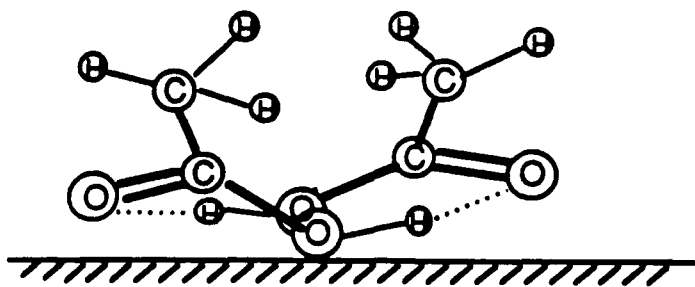


fig. 10



Table 1. Acetate Vibrational mode assignments

	CH <sub>3</sub> COO <sup>-</sup> (CD <sub>3</sub> COO <sup>-</sup> ) [32]		Cu(100) [8]		Al(111) [11]		Pt(111) [8]	Pt(111) [this work]	
$\nu_{CH}$	2935	(2111)	3000	(2218)	3025	(2260)	—	2930 -2988	(2261, 2203)
$\nu_{aCOO}$	1556	(1545)	—	—	—	—	—	—	—
$\nu_{sCOO}$	1413	(1406)	1434	(1413)	1470	(1470)	1400	1398	(1388)
$\delta_{CH_3}$	1344	(1085)	—	—	—	—	—	1340 <sup>os</sup>	(903)
$\nu_{C-C}$	926	(883)	1041	(1061)	1055	(1070)	—	1000	(1049)
$\delta_{COO}$	650	(619)	677	(648)	695	(655)	665	671	(661)
$\rho_{COO}$	471	(419)	—	—	—	—	—	463	(428)
$\nu_{M-O}$	—	—	339	(308)	425	(410)	300	302	(225)

os: Off-specular observation

Table 2. Acetic Acid Vibrational mode assignments

	$\text{CH}_3\text{COOH}_{(g)}$ [32]	$(\text{CD}_3\text{COOH}_{(g)})$	$\text{CH}_3\text{COOH}_{(s)}$ [38]	$(\text{CD}_3\text{COOH}_{(s)})$	$\text{Al}(111)$ [11]	$\text{Pt}(111)$ [this work]
$\nu_{\text{CH}}$	3030	(2128)	—	(22780, 2116)	3030 (2275, 2155)	2927 (2252, 2174)
$\nu_{\text{OH}}$	3125	(3100)	2875	(2852)	2740 (2740)	2988 (2425)
$\nu_{\text{C=O}}$	1739	(1730)	1648	(1641)	1730 (1730)	1675 (1640)
$\delta_{\text{CH}_3}$	1387	(1075)	1439	(1035, 1055)	1400 (1050)	1400 (913)
$\nu_{\text{C-O}}$	1282	(1220)	1284	(1287)	1350 (1310)	1318 <sup>os</sup> —
$\delta_{\text{OH}}$	1186	(1156)	1418	(1404)	990 (945)	1176 (1176)
$\rho_{\text{CH}_3}$	—	—	1049	(920)	—	1034 (903)
$\nu_{\text{C-C}}$	—	—	908	(856)	—	1034 (1039)
$\gamma_{\text{OH}}$	—	—	923	(920)	—	932 (913)

os: Off-specular observation